

Organic Light Emitting Diodes

Developing Chemicals to Light the Future

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New platinum-group metal complexes have surprising potential for smaller, lighter, and more energy-efficient flat-panel displays.

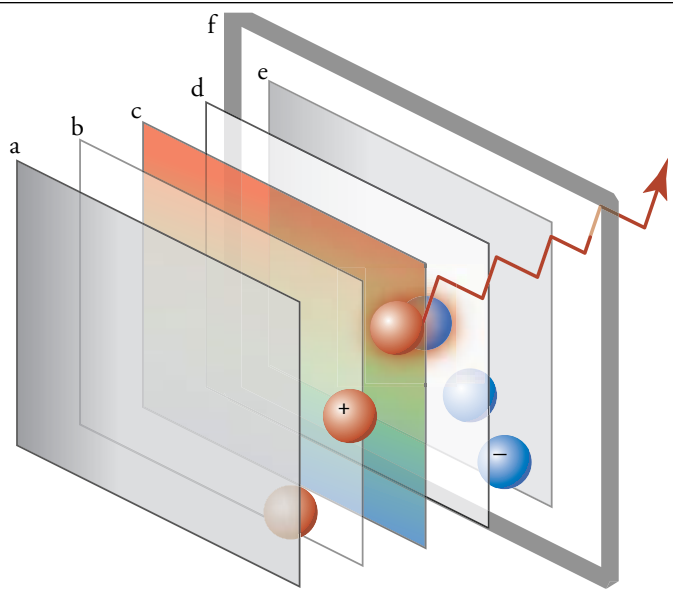
The demand for flat, lightweight television and computer displays has given rise to many different flat-panel display technologies. Recently, much emphasis has been placed on organic light emitting diodes (OLEDs), chemical systems which have the potential to be not only smaller and lighter, but also more energy efficient than other current display technologies.¹ The most common form of television and computer displays now in use are cathode ray tubes, often referred to as CRTs. These devices accelerate electrons (cathode rays) through an electrical potential until they strike a certain area on a screen. Attached to this screen are phosphors (luminescent compounds) that emit a photon (or "particle") of light when the electron strikes it. The color contrast and

resolution from a CRT is very good, but the device is bulky and thus impractical for portable and lightweight applications. The current technology used in portable televisions and lap top computers is liquid crystal displays (LCDs). These displays utilize liquid crystals, compounds that align in certain conformations when an electric potential is placed across them, to create an image on a screen. Aligning the crystals with electricity is very energy efficient, but LCDs require a great deal of energy to back-light the display in order to make the image visible. The high energy input required to back-light the display makes the LCD screen very inefficient, and consequently many portable devices that utilize this technology, like lap top computers, have short battery lives.

OLEDs make use of a phenomenon

known as electroluminescence in which electronically excited materials emit light. An OLED consists of three basic layers of different chemical compounds sandwiched between an anode and a cathode (Fig. 1). When an electric current passes through the diode (from cathode to anode), electrons and holes (units of positive charge) travel through their respective transport layers until they recombine in the light-emitting layer. This process is called light-emitting charge recombination.² The light-emitting layer contains the electroluminescent material, which emits photons that produce the visible image on a screen. The materials that occupy the light-emitting layer of the OLED must luminesce a desired wavelength so that a full range of colors can be created on a display. These considerations

Figure 1. An OLED consists of three basic layers of different chemical compounds sandwiched between an anode (a) and a cathode (e). When an electronic current passes through the diode, electrons (blue spheres) and holes (units of positive charge, red spheres) travel through their respective transport layers (b, d) until they combine in the light-emitting layer (c). The OLED is fused to a glass plate (f), the front of the screen.



have prompted research chemists to examine new luminescent transition metal complexes with long-lived excited state and solid state luminescence, such as platinum group systems, as potential materials for OLEDs.

Platinum group metals are those elements located near platinum on the periodic table, such as iridium and gold. In compounds, these elements tend to adopt electronic configurations similar to that of platinum, which gives them similar chemical reactivity. Emission from these complex-

es generally involves transfer of an electron from an orbital on the metal to an orbital associated with the ligand (*i.e.*, the molecule bound to the metal). This type of electronic excitation is referred to as a metal-to-ligand charge transfer (MLCT). Ligands possessing low lying π^* orbitals, such as dithiolates and diimines, are usually involved in these types of transitions because the energy of their lowest unoccupied molecular orbital (LUMO) is comparable to that of the metal. The directionality of charge transfer in these

systems is normally assigned as (metal) $d \rightarrow$ (ligand) π^* , although the nature of the highest occupied molecular orbital (HOMO) may not be entirely d -orbital (metal) in character.³ Consequently, the energy of the MLCT excited state is sensitive to both the bonding character of the acceptor ligand and the electronic environment around the metal.

The ligands that surround the metal play a significant role in modifying the energy of the complex's excited state; it is the energy of the excited state that accounts for the color and intensity of the luminescence. The ability to tune this excited state by varying the types of ligands has produced many compounds with emission energies spanning the visible spectrum. Many of these compounds are already used to manufacture simple devices, and the number of OLEDs containing platinum group complexes continues to grow.⁴

FROM LIGANDS TO LIGHT

My work in the Eisenberg Group Laboratory at the University of Rochester has focused on the photochemistry of square planar platinum group complexes. Emission from these systems has been observed in both solution and the solid state. The solid state luminescence of iridium (I) dithiolate complexes has been particularly interesting from the standpoint of possible OLED materials. In complexes containing the *mnt* (maleonitriledithiolate) ligand, emission from this charge transfer gives rise to intense luminescence in the solid state and in frozen glass media. Previous reports of these systems involved complexes of the type $[\text{Ir}(\text{CO})\text{L}(\text{mnt})]^-$, where L (ligand) represents either CO (**1**) or PPh_3 (**2**) (Fig. 4).³

The focus of the present investigation was to prepare a series of iridium (I) dithiolate complexes with hopes of tuning the emission energy by varying the dithiolate and L-type ligand. Our research has been successful and we have characterized a series of new iridium dithiolate complexes and examined their emission energy. Systems involving dithiolates other than *mnt* were found to be non-emissive, while complexes of *mnt* containing different monodentate phosphine ligands were found to display intense solid state luminescence. The luminescence is tunable through approximately 25 nm in the red region of the electromagnetic spectrum, which is consis-

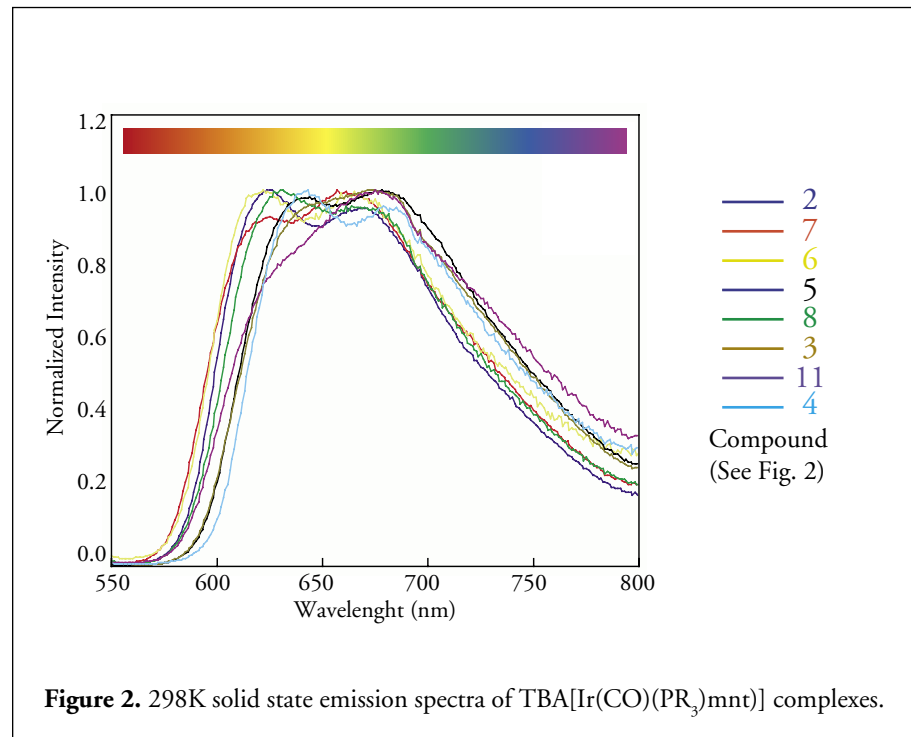


Figure 2. 298K solid state emission spectra of $\text{TBA}[\text{Ir}(\text{CO})(\text{PR}_3)\text{mnt}]$ complexes.

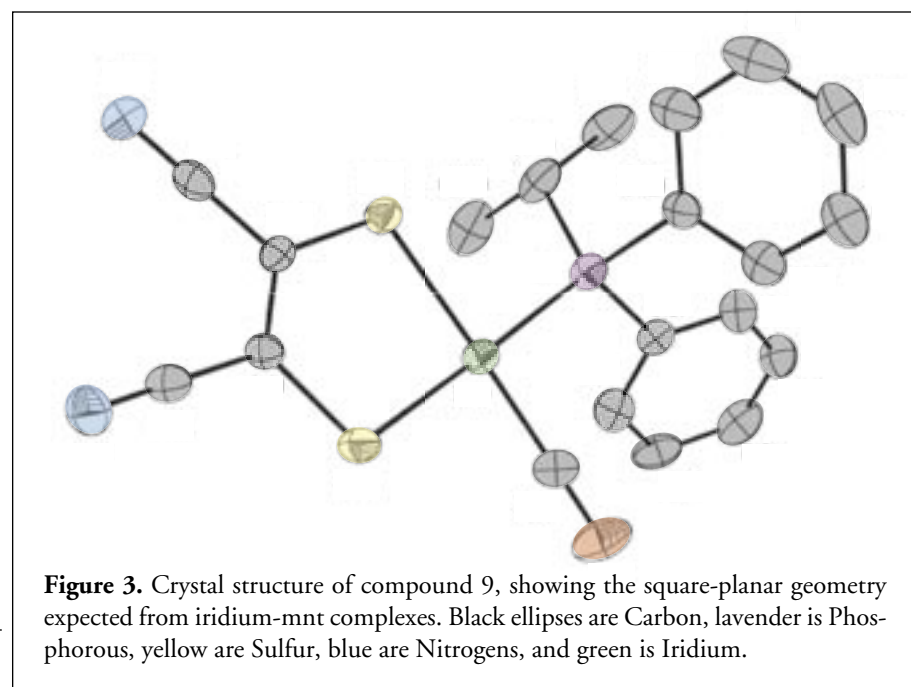


Figure 3. Crystal structure of compound **9**, showing the square-planar geometry expected from iridium-*mnt* complexes. Black ellipses are Carbon, lavender is Phosphorous, yellow are Sulfur, blue are Nitrogens, and green is Iridium.

tent with the electron donating capacity of the phosphine ligand. These results are promising and suggest that mnt complexes may be a viable option in developing OLED technology.

COMPLEX LUMINESCENCE

Our research examined 15 complexes that are similar in structure and composition to two previously reported iridium (I) dithiolate complexes (Fig. 4).³ Compounds **1** and **2** had been reported previously and were used as a template for the synthesis of **3** - **11**. The new dithiolate complexes, *tdt*, *ecda*, and *dmit* (**12** - **17**) were prepared in similar fashion to compound **1** with slight variations.

Compounds **3** - **11** exhibit solid state luminescence similar to complex **1**. However, the other dithiolate complexes failed to show any luminescent properties in the solid state, which may be attributed to the energy of the π^* orbitals in these complexes. The mnt ligand appears to be the most electron-withdrawing of the dithiolate ligands studied. Consequently, its π^* orbitals are closer in energy to the metal *d*-orbitals than the other dithiolates. The stretching frequency of the carbonyl bonds (CO) in the $[\text{Ir}(\text{CO})_2(\text{mnt})]^-$ complex vibrate at higher a frequency than the corresponding bonds in compounds **12**, **14**, and **16**, indicating that there is substantially less electron donation from the metal. Such a situation arises when the metal is made more electron deficient by means of an electron-withdrawing ligand (in this case, the mnt ligand). With the other dithiolates, the electron-withdrawing character is less, and the energy of the π^* orbital may be elevated to such an extent that the highest energy metal orbital ($d_{x^2-y^2}$) of the iridium falls below that of the dithiolate. In this situation, the MLCT transition may not be observed to the same extent as in the mnt complexes, and weakly emissive ligand field transitions (transitions between metal orbitals) may dominate.

We hypothesized that the electronic character of the phosphine ligand would partially determine the electron density surrounding the iridium center for compounds **3**-**11**. By varying the phosphine R-groups (R = Me, Ph, tolyl, etc.), the energy of the metal-based HOMO could be changed in such a way as to produce a series of luminescent compounds with predictable emission energies, and therefore predictable colors. Results from room temperature emission

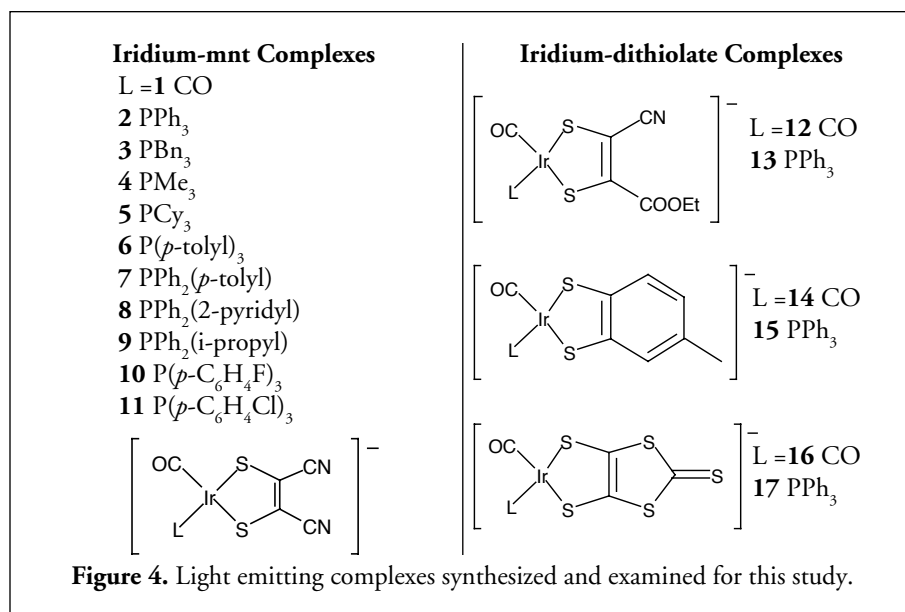


Figure 4. Light emitting complexes synthesized and examined for this study.

measurements in the solid state indicate that the emission energies of the complexes are, to some degree, controllable. Emission maxima for the compounds encompass a range of 25 nm, which corresponds to an energy difference of approximately 500 cm⁻¹ (approximately 6 kJ/mol) (Fig. 2). The reddest emissions come from the compounds containing aliphatic phosphine ligands, (**3,4** and **5**) as expected from a simple assessment of the electron-donating capacity of each phosphine ligand. Aliphatic phosphines are better able to donate electrons to the metal orbitals and increase the energy of the HOMO (d_{xy}), which causes a red-shifted (lower energy) emission. In contrast to aliphatic phosphines, the aromatic phosphines are less efficient electron donors and tend to decrease the relative energy of the HOMO leading to a slightly more blue-shifted (higher energy) emission (Table 1).

All of the $[\text{Ir}(\text{CO})(\text{PR}_3)(\text{mnt})]^-$ compounds (**3** - **11**) synthesized are yellow or yellow-orange powders. A crystal structure of compound **9** was elucidated, which showed the expected square planar geometry (Fig. 3). The compounds appear stable in the solid state for months if kept in a sealed vial. However, the complexes begin to turn orange after extended exposure to air, which is probably due to oxidation of the phosphine part of the complex. The compounds decompose rapidly in solution, changing color from yellow to deep orange in a matter of minutes. Although this decomposition might appear problematic, the mnt compounds do not exhibit any luminescence when in solution, so their

chemical instability does not pose any serious problems to their potential industrial application.

CONCLUSION

We have synthesized thin films of these compounds by preparing a solution of 90% dichloromethane, 9% polycarbonate, and 1% metal complex, and then applying this polymer to a glass slide. The films exhibit the characteristic luminescence of the solid compounds, which is encouraging because incorporating the metal complex into a polymer (doping) is one of the chief means toward industrial application. The doped polymer films can be coated onto a glass surface to create a device that contains an evenly distributed amount of the luminescent material.

The results presented here demonstrate that luminescent compounds with predictable excited state energies can be produced successfully. Bolstered by this knowledge, chemists can produce more highly emissive and thermally stable compounds with the properties necessary for complete display manufacture. With new compounds such as these iridium complexes, the OLED industry can press forward and create the displays that will light the future. □

Zachary Tonzetich graduated from the University of Rochester in 2002 with a B.S. in Chemistry. His work on luminescent transition metal complexes for OLED applications was part of his senior thesis work under Professor Richard Eisenberg. He is a National Science Foundation predoctoral fellow currently working toward his Ph.D. in inorganic chemistry at the Massachusetts Institute of Technology.